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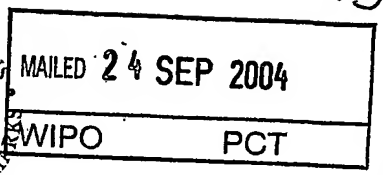

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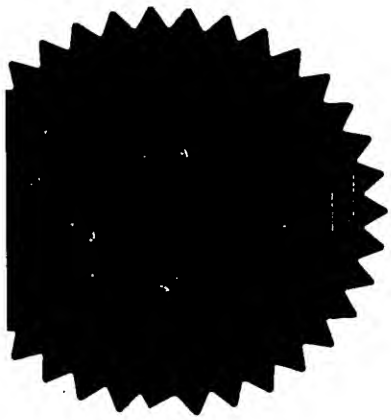

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1. Your reference — NT/46592.GB01 26AUG03 E832782-1 D01631 P01/7700 0.00-0319929.6

2. Patent application number *(The Patent Office will fill in this part)* — 0319929.6

3. Full name, address and postcode of the or of each applicant *(underline all surnames)*

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Jaquet-Droz 1
CH-2007 Neuchâtel
Switzerland

Patents ADP number *(if you know it)* — 8062101001

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4. Title of the invention — Yarn and Textile Products

5. Full name, address and postcode in the United Kingdom to which all correspondence relating to this form and translation should be sent

Reddie & Grose
16 Theobalds Road
LONDON
WC1X 8PL

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46592.GB01

Yarn and Textile Products

FIELD OF THE INVENTION

The present invention relates to the chemical and biochemical functionalization of yarn and textile products by applying linker polymer mediated chemistries for post-process attachment of any type of molecular species to yarns and textiles.

BACKGROUND OF THE INVENTION

Advanced textile technology focuses on integrating desired non-textile functions in the production steps such as yarn spinning, yarn finishing, post-weaving textile treatment and cloth treatment. However, most current yarn and textile production processes are not compatible with requirements implied by biological components such as enzymes and protein or carbohydrates. Therefore, the addition of new bio-based functions to textile materials, in particular textile functionalization with biologically active substances, is difficult to attain. Biologically active agents used to date for textile functionalization are preferably inorganic or organic in nature. Inorganic and organic materials generally conform with yarn and textile production conditions.

A representative example of an inorganic, biologically active agent is the inclusion of metallic material in textiles. The antibacterial activity of metals such as silver, copper, mercury and zink are well documented. In contrast to antibiotics, bacteria do not acquire resistance to these bactericidal agents. Silver is generally a safe and effective antimicrobial metal. Silver ions function in adversely affecting cellular metabolism to inhibit bacterial cell growth. When absorbed into bacterial cells, silver ions suppress respiration, basal metabolism of the electron transport system, and transport of nutrients through microbial cell membranes. Silver ions also inhibit bacterial growth by producing active oxygen on the surface of silver powder and silver-plated articles.

U.S. Pat. No 6,379,712 discloses a procedure for the encapsulation of metallic nanoparticles in a plant extract and documents widespread antimicrobial activity of the product. U.S. Pat. No 5,709,870 discloses a silver containing antimicrobial agent

comprising a silver salt of carboxymethylcellulose and having a degree of substitution of carboxymethyl groups of not less than 0.4. Japanese patent No. 3-136649 discloses an antibacterial cloth to be used for washing the udders of milk cows. The silver ions from silver nitrate were crosslinked with polyacrylonitirile. The cloth had anti-bacterial activity on six bacteria including streptococcus and staphyloccus.

Quaternary ammonium salts are cited here as examples of organic molecules that affect microbial growth and proliferation. Either as low molecular weight components or as polymers, quaternary ammonium salts have been included into yarns and textile products and antimicrobial activity of this class of agents has been demonstrated. U.S. Pat. No 6,436,419 teaches that bonding of "quats" on a substrate such as textiles results in a durable, safe, antibacterial treatment. Moreover, U.S. Pat. No. 6,306,835 communicates that 3-trimethylammonium-2-hydroxypropyl-N-chitosan, a quaternary ammonium derivative of natural polymers such as chitosan exhibit antimicrobial activity at low concentrations.

Lysozyme is a muraminidase with basic character which is widely distributed in nature. Its antibacterial activity is strongly related to its catalytic properties that affect Gram-positive bacteria. It has further been suggested, that lysozyme in its dimeric form, exhibits bacteriostatic properties towards both Gram-positive and Gram-negative bacteria. Antimicrobial activity was retained with a lysozyme-dextran conjugate whereby the lysozyme is suggestedly linked to dextran at the reducing end of the polysaccharide (S. Nakamura, A. Kato, K. Kobayashi. J. Agric. Food. Chem. 1991, 39, 647-650).

Many natural or synthetic yarns and textile products do not provide the physical predisposition or chemical properties for modifications. Synthetic yarn endures harsh chemical treatment, regarding temperatures and solvents, during the spinning process or during chemical post-spinning treatment. Post-spinning processes are for instance i) dyeing and associated curing of dyed yarns, ii) post-spinning fiber texturation, or iii) cleaning of natural and synthetic yarns and textiles. Moreover, most of these processes are batch processes and are not locally applicable.

The linker molecule concept presented here is one approach to overcome the limitations of current yarn, textile and cloth processing. The concept consists of binding linker molecules to textiles in a one-step process or in a sequential two-step process. Linker molecules are multiple (preferably more than two) substituted

polymeric chemicals, whereby the said substitutions are thermochemical or photochemical activatable functions allowing, upon activation, the formation of covalent bonds with molecular species to be attached to materials or textile fibers. In comparison to current direct chemical derivatization of yarns and textile products by batch processing, linker polymers with addressable chemical reactivity, may add beneficial physical and chemical characteristics to the textile. Yarn and textile modification with linker polymers allow changing surface charge or surface polarity or both, and opens the scope of applicable secondary modification chemistries which may be thermochemical or photochemical.

The chemical modification of non-metallic surfaces and materials to achieve desired chemical and physical surface characteristics and to achieve covalent binding of biomolecules have been described in EP 0484 472 (incorporated herein by reference). The teachings relate to surface modification by the use of latent reactive groups to achieve covalent coupling of reagents such as biomolecules to various material substrates with derivatized biopolymers (US Pat. No. 5,563, 056 and DE 19818360). The preferred latent reactive group is typically described as a photochemically reactive functional group (i.e. a photoreactive group). When exposed to an appropriate energy source, a photoreactive group undergoes a transition from an inactive state to a reactive intermediate capable of forming covalent bonds with appropriate materials or molecules. Such linking agents, in particular photolinker polymers that are multiple substituted with photoreactive groups can be used for either attaching non-reactive compounds to a surface or for priming a relatively inert surface to render it reactive upon exposure to suitable actinic radiation.

Further to the above, the fact that most yarn and textile production and dying processes are bound to high temperatures leaves a very restricted window of chemical reaction conditions open for introducing biochemical functions to textiles, such as for instance enzyme catalyzed biochemical reactions or biospecific intermolecular binding events that depend on correct folding of the biomolecules. Choice and chemical nature of the linker polymer may thus be decisive for successful immobilization of (catalytically) active or target binding biomolecules on yarn and textile-based materials.

BRIEF DESCRIPTION OF THE INVENTION

It is, therefore, an object of the present invention to provide a process for effectively immobilizing biomolecules on yarn and textile products retaining their biological activity. Bioactivity of biomolecules presumes proper folding and intact 3-D structure of the biomolecules even after immobilization. Intramolecular and intermolecular hydrogen bonds are essential elements sustaining 3-D structured domains in biomolecules, particularly in catalytically active enzymes, target-binding proteins and glycoproteins. Such requirements are fulfilled by using protein-based or polysaccharide-based linker polymers for textile functionalization with biomolecules.

It has now been found that the above-described and other objects of the present invention are attained by post-process treatment of yarn and textile with carbene generating linker polymers on the basis of chemically derivatized biopolymers. Post-process carbene mediated functionalization of yarn and textile is effective in attaching antimicrobial agents including low molecular substances and bioactive reagents in general.

Another object of the invention is to provide a process leading to products allowing the unrestricted covalent attachment of low and high molecular weight substances to yarns and textiles.

A further object of the present invention is to provide processes and products leading to controlled release of immobilized species from functionalized yarns and textile products.

An even further object of the invention is the making of a textile product with antibiotic properties.

These and other objects of the present invention will become apparent from the following detailed description.

This invention teaches generic procedures for the functionalization of yarn and textiles, and products resulting thereof with any type of molecular species - including biologically active substances - and any type of natural or synthetic yarn. In preferred embodiments of the invention, textile or yarn is post-process treated with linker polymers able to generate carbenes. Carbene generating linker polymers include

molecules and molecular conjugates that selectively alter the chemical, physical and biochemical properties of target yarns and textiles. Such treatment may alter the bioresponse of textile products, or introduce novel bioactivity features to textile products. Post-process carbene mediated functionalization of yarn and textile is effective in attaching low molecular components by direct or by linker polymer mediated immobilization. Appropriate choice of the linker polymer in conjunction with specific catalytic cleavage of the linker polymer, enables controlled release of bioactive chemical species.

According to the invention there is provided a method of providing a yarn or textile product with a desired property which comprises:

contacting a linker molecule comprising two or more activatable chemical groups with a yarn or textile product, and a non-linker molecule having a desired property;

activating the activatable chemical groups of the linker molecule to cause covalent attachment of the linker molecule to the yarn or textile product and the non-linker molecule, thereby attaching the non-linker molecule to the yarn or textile product by means of the linker molecule, and providing the yarn or textile product with the property of the non-linker molecule.

The linker molecule, the yarn or textile product, and the non-linker molecule may be contacted in any order. Preferably the linker molecule is contacted with the yarn or textile product before the non-linker molecule.

According to the invention there is also provided a yarn or textile product covalently attached, by means of a linker molecule, to a non-linker molecule having a desired property, thereby providing the yarn or textile product with the desired property.

There is further provided according to the invention a linker molecule comprising two or more activatable chemical groups to allow covalent attachment of the linker molecule to a yarn or textile product and a non-linker molecule having a desired property thereby attaching the non-linker molecule to the yarn or textile product by means of the linker molecule, and providing the yarn or textile product with the property of the non-linker molecule.

The non-linker molecule may be a solvent, a synthetic or natural chemical, a synthetic or natural dye, a synthetic polymer, a biopolymer, a biomolecule, a biologically active molecule, a synthetic or natural vitamin or hormone, or any combination thereof.

Preferably the non-linker molecule is an enzyme (such as lysozyme), a growth factor, an anti-microbial agent, an antibiotic, a fungicide, an agent capable of suppressing the proliferation of bacteria or fungi, or any combination thereof.

The linker molecule may further comprise one or more functional groups having a desired property different to the property of the non-linker molecule, so that covalent attachment of the linker molecule to the yarn or textile product additionally provides the yarn or textile product with the property of the, or each functional group.

There is also provided according to the invention a method of providing a yarn or textile product with a desired property which comprises:

contacting a linker molecule comprising one or more activatable chemical groups, and one or more functional groups having a desired property, with a yarn or textile product;

activating the activatable chemical group or groups of the linker molecule to cause covalent attachment of the linker molecule to the yarn or textile product, thereby providing the yarn or textile product with the property of the functional group(s) of the linker molecule.

There is further provided according to the invention a yarn or textile product covalently attached to a linker molecule, the linker molecule comprising one or more functional groups having a desired property, thereby providing the yarn or textile product with the desired property.

There is also provided according to the invention a linker molecule comprising one or more activatable chemical groups to allow covalent attachment of the linker molecule to a yarn or textile product, and one or more functional groups having a desired

property, so that covalent attachment of the linker molecule to the yarn or textile product provides the yarn or textile product with the property of the functional group(s) of the linker molecule.

Preferably the, or each functional group is a positively charged group at neutral pH (such an amino group), a negatively charged group at neutral pH (such as a carboxyl group), a thiol group, or a dye such as a fluorescent dye. If the, or each functional group is negatively charged, methods of the invention may further comprise contacting the yarn or textile product with positively charged metal ions, preferably silver ions, to bind the metal ions to the functional group or groups. Metal ions such as silver ions have antibacterial action. Thus, these embodiments allow the antibacterial action of metal ions to be combined with the desired property of the non-linker molecule. Preferably the metal ions are contacted with the yarn or textile product before the linker molecule.

Preferably the linker molecule is multiply substituted with activatable chemical groups.

Preferably activation of the, or each activatable chemical group of the linker molecule generates a carbene intermediate.

Preferably the, or each activatable chemical group is activated with actinic energy and converts to a highly reactive intermediate.

Preferably the, or each activatable chemical group of the linker molecule is thermochemically or photochemically activatable.

Preferred photoactivatable chemical groups are aryldiazirines. These compounds are precursors for photogenerated carbenes. Other preferred photoactivatable chemical groups are members of the benzophenone family, benzophenone being the moiety that generates reactive intermediates. Further photoactivatable chemical groups include arylazides. However, these are less preferred because they are less efficient and require difficult handling conditions.

The linker molecule preferably comprises a natural or synthetic polymer, preferably a biopolymer. Suitable linker molecules comprise a protein, peptide, or polysaccharide, or a dextran-based polymer.

In preferred embodiments the linker molecule comprises a cleavage site which is cleaved under predetermined conditions to release the non-linker molecule or functional group from the yarn or textile product. This allows controlled release of the non-linker molecule or functional group from the yarn or textile product. For example, the linker molecule may comprise a target for a hydrolytic enzyme to allow enzyme-induced, or biosystem-induced release of the non-linker molecule or functional group. The following are suitable examples:

i) the linker molecule comprises a substrate for an endoglycosidase, or an endopeptidase;

ii) the linker molecule is a dextran-based biopolymer which comprises a target for a dextranase;

iii) the linker molecule is a hyaluronic acid-based biopolymer which comprises a target for a hyaluronidase;

iv) the linker molecule is a protein-based polymer which comprises a target for a protease;

v) the linker molecule is a peptide-based polymer which comprises a target for an endopeptidase.

The textile product may be of natural or synthetic origin, a blend of synthetic yarns, or a blend of natural and synthetic yarns.

In some circumstances, it may be desirable to pre-treat the yarn or textile product to improve its wetting properties so that the linker molecule can adsorb to the surface of the yarn or textile product. For example, commercial synthetic polyester yarn has low water adsorption and wetting properties and so may be pre-treated with oxygen plasma.

There is further provided according to the invention use of a linker molecule of the invention to covalently attach a non-linker molecule having a desired property and/or a functional group having a different desired property to a yarn or textile product, thereby providing the yarn or textile product with the desired property or properties.

There is also provided according to the invention a composition comprising a yarn or textile product, a linker molecule of the invention, and optionally a non-linker molecule.

BRIEF DESCRIPTION OF DRAWINGS

Fig. 1 shows the optical microscopy image (Fig 1A) and fluorescence microscopy image (Fig. 1B) of polyester textile treated with the linker polymer (OptoDex) or dye-labeled (fluorescent) Cy3-OptoDex.

Fig. 2 is a quantitative analysis of linker polymer mediated enzyme immobilized on woven textile showing the light dependence and linker polymer dependence of the process. The enzyme immobilized is alkaline phosphatase; PES corresponds to a polyester control sample

Fig. 3 depicts the linker polymer mediated immobilization of the enzyme lysozyme. The enzymatic activity monitors the disruption of fluorophore labeled bacteria. High fluorescence intensity corresponds to a high lytic activity of lysozyme. PES corresponds to a polyester control sample

Fig. 4 shows the feasibility of combining two bactericidal agents: metallic silver and lysozyme on textile as tested by the lytic activity. As bactericidal Ag+ ions do not break the cells and metallic silver quenches fluorescence to some extent, the lytic activity of immobilized is not fully detected. PES corresponds to a polyester control sample; Ag refers to treatment of textiles with metallic silver.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The generic process of covalent chemical functionalization with linker polymers allows attachment of dyes, polymers, biomolecules, inorganic materials to textile of any shape and dimension at any state in product manufacturing. A first part of the invention concerns the use of linker polymers, whereby the linker polymers are multiple substituted with chemical functional groups that convert to highly reactive intermediates when activated with actinic energy. Preferred linker polymer base material are polysaccharides or proteins. Polar domains of proteins and in particular polysaccharides bind water molecules and thus provide chemical features for hydrogen bonding. Attached as linker polymers to yarn or textile material surfaces, polysaccharides make the surfaces homogeneously hydrophilic, suppress non-specific adsorption of system components and generate a high degree of biocompatibility.

In chemical terms, the natures of the linker polymers are either proteins or polysaccharides. Proteins, such as for instance bovine serum albumin can be multiple derivatized at the epsilon amino functions of lysine residues with organic isothiocyanates or other amine derivatizing chemical crosslinkers. In this sense, any type of protein that is composed of more than two lysine amino acid residues may be used as protein-based linker polymer. This also includes synthetic polypeptides or genetically engineered and recombinant proteins. Depending on the use of the modified textile, it may be of advantage to utilize designed protein-based linker polymers: proteins that include for instance thermostability principles or protein sequences that include amino acid sequences that are uniquely recognized and catalytically cleaved by specific proteases, if enzyme-induced release of the immobilized bioactive species is envisaged.

Another preferred type of linker polymer is based on polysaccharides, for example dextrans or hyaluronic acid among many others. Dextran can be chemically modified in that a defined number of polymer constituting glucose molecules are chemically opened at vicinal hydroxyl functions. Generated aldehydes are then further derivatized into amino functions leading to amino dextran as a base for functionalization with amine reactive photoactive bifunctional crosslinkers. It becomes evident that the size of the dextran molecule (corresponding to its molecular weight) is not limiting to the approach, and any type of dextran or polyglycan may serve as base for the production of photolinker polymers. Moreover, the more glucose molecules are finally derivatized with the linker unit, the higher is the probability of forming densely crosslinked polymers. Formation of linker polymers from hyaluronic

acid follows a similar strategy: the acetylated amino sugars are chemically or enzymatically deacetylated. The products of such treatment are polysaccharide based polymers presenting reactive amino groups for thiocarbamoylation reactions for instance. As with the dextran mentioned above, the molecular weight or chain length of the hyaluronic acid is not limiting.

Endoglycosidases as for instance dextranase, cellulase, glucanase or hyaluronidase can be used to cleave the polysaccharide-based linker polymers either to tailor the molecular size of the starting material or to catalytically cleave immobilized molecular species effecting timed release. Analogously, sequence specific proteases, for instance asparaginase, pectinase or protease (*Aspergillus niger*), may serve to selectively cleave protein- or peptide-based linker polymers. Moreover, covalent and non-covalent assemblies of enzymes and target-binding proteins with polysaccharides or proteins show improved long-term stability.

Another aspect of the invention concerns the synthesis and use of linker polymers that carry functional groups, in addition to the photoactivatable functions. Limited substitution with hetero-bifunctional photocrosslinkers leads to a linker polymer with free amino groups. Such a derivative is called OptoDex A (Opto for optical activatable, Dex for dextran and A for amine functions). Treatment of these amino groups in a second reaction with an anhydride - for instance with glutaranhydride - leads to a linker polymer with free carboxyl functions. Such derivatives are negatively charged at neutral pH. The product is called OptoDex C (Opto for optical activatable, Dex for dextran and C for available carboxyl groups). In analogy to the negatively charged linker polymer, a photoactivatable linker polymer can been synthesized by derivatization of OptoDex A with an activated fluorophore such as a N-hydroxysuccinimide ester of the cyanine dye Cy3 or Cy5. Products of such modifications are fluorescent photoactivatable linker polymers, the fluorescent properties of which are in accordance with the parent fluorophores Cy3 and Cy5 respectively. Cy3-OptoDex or Cy5-OptoDex serves as examples for the covalent attachment of dyes (here fluorescent) to yarns and textiles, the covalent link between the textile and the linker polymer being effected by irradiation with light.

Still another aspect of the invention concerns the chemical nature of the yarn or textile product. As carbenes form covalent bonds with all materials except metals, all yarn and textile materials except metallic wires can be functionalized by the linker polymers mentioned. Included are synthetic yarns such as polyamide, polyester,

mylar, and others, as well as natural fibers and textile such as cotton and silk among others. The process of textile functionalization is also applicable with blended yarns and textile blend products. It is noteworthy that such functionalization can be carried out at any step of textile processing.

Still another aspect of the invention concerns the application of the process for yarn and textile dyeing and physico-chemical functionalization. Processes described can be used for textile or yarn dyeing either by a procedure as detailed in example 1 or by applying a mixture of linker polymer and the dye. The dye molecules are covalently bound to the textile samples upon activation of the latent carbene generating functions with light or at elevated temperatures (75 to 120°C)

Mere attachment of linker polymers to yarns or textile changes the physical properties depending on the characteristics of the linker polymer chosen. The surface charge of yarns can be deliberately adjusted by simply attaching linker polymers carrying either amino groups (positively charged at neutral pH) or carboxyl groups (negatively charged at neutral pH) for example.

A most attractive feature of the invention is the covalent attachment of biomolecules to textiles. There is no limitation with respect of type or size of biomolecules to be immobilized, however small probe molecules may request linker polymers with a high degree of substitution with photoactivatable groups, as probe molecule binding occurs statistically. Representative of the many types of molecules that can be immobilized by procedures described herein, example 3 and example 4 document the immobilization of the enzymes alkaline phosphatase and lysozyme, respectively. Lysozyme is a muraminidase which is widely distributed in nature. Its antibacterial activity is related to its catalytic properties by breaking the cell wall components of Gram-positive bacteria. In its polymeric state or as a dextran conjugate, lysozyme reveals antimicrobial activity for both Gram-negative and Gram-positive bacteria. Teachings of example 4 evidence the generation of textile with antibiotic properties. Needless to mention that this and all textile modifications mentioned before are addressable with light. Pattern deposition of color or specific biological reagents thus becomes feasible by applying the teachings of this invention.

A further potential of the processes described is substantiated by the experiment detailed in example 5. Using lysozyme as immoblized component and a dextran-based linker polymer, the results of example 5 evidence that the linker polymer is

accessible to the enzyme dextranase. The hydrolytic action of the enzyme leads to a release of the immoblized enzyme. The experiment documents further that it is the linker polymer that is responsible for retention of lysozyme on the textile sample.

In another aspect the invention teaches the combination of polymer mediated immobilization of bioactive substances with the antibacterial action of metals as for instance silver and others. In such systems, metallic silver is deposited on woven textile, followed by coating with the linker polymer OptoDex. In one embodiment, a linker polymer providing negative charges, for instance OptoDex C may be selected, to ascertain the binding and retarded release of bioactive Ag^+ Ions, as liberated from metallic silver in biological environments. In a further preferred embodiment silver (antimicrobial) and linker polymer coated textile is combined with a second antibacterial agent, for instance lysozyme as example, in order to increase the antimicrobial effect of the textile finishing and broaden the scope of antimicrobial activity of the product. An approach as described here is detailed in example 6.

Application of the procedures and resulting products are manifold. Functionalization of yarn and textile is of use in dyeing of fabrics and cloths. In this application linker polymers with photoactive functions provide the basis for local attachment of bioactive agents or dyes. Linker polymer mediated immobilization of antimicrobial and antibacterial agent leads to products with desired properties for application in medicine and specifically in the treatment of wounds.

Various aspects of the invention are defined in the following paragraphs:

1. Yarn, textile and textile products post-processing functionalised by covalent bonding linker molecules, preferably carbene generating linker polymers, and non-linker molecular species, whereby the combination of the linker molecule and non-linker molecular species generate new physical, chemical properties of the base material and tailored biochemical interactions with biosystems.

2. Textiles and textile products as described in paragraph 1 whereby the textile material is of natural or synthetic origin, blends synthetic yarns, blends of natural and synthetic yarns, and textile products made of blended yarns.

3. Yarn, textile and textile products as described in paragraphs 1 and 2, wherein the linker molecules are natural or synthetic polymers multiple substituted with thermochemically or photochemically activatable chemical functions.

4. Yarn, textile and textile products as described in paragraphs 1 to 3, wherein the linker molecules are proteins, peptides or polysaccharides and the generated chemically reactive functions are carbene intermediates.

5. Yarn, textile and textile products as described in paragraphs 1 to 4 wherein the non-linker molecular species are solvents, synthetic or natural chemicals, synthetic polymers, biopolymers, biomolecules or combinations thereof.

6. Yarn, textile and textile products as described in paragraphs 1 to 5, wherein the non-linker molecular species are synthetic or natural dyes.

7. Yarn, textile and textile products as described in paragraphs 1 to 6 with linker molecules and biologically active molecules that actively interact with biological systems by effecting activation, regulation or inhibition of biosystem components.

8. Yarn, textile and textile products as described in paragraphs 1 to 7, wherein the non-linker molecular species are enzymes, growth factors, anti-microbial agents, antibiotics, fungicides or combinations thereof.

9. Yarn, textiles and textile products as described in paragraphs 1 to 8 whereby the photolinker polymer is a dextran-based photolinker polymer and the biologically active molecule is lysozyme.

10. Yarn, textile and textile products as described in paragraphs 1 to 9, wherein the non-linker molecular species are synthetic or natural vitamins or hormones.

11. Yarn, textile and textile products as described in paragraphs 1 to 10, whereby the linker molecules are targets of hydrolytic enzymes allowing enzyme-induced, or biosystem-induced release of biologically active non-linker molecules.

12. Textiles and textile products as described in paragraphs 1 to 11 whereby the linker molecule is a substrate for endoglycosidases, or a substrate for endopeptidases.

13. Textiles and textile products as described in paragraphs 1 to 12 whereby the linker molecule is a dextran-based biopolymer and the hydrolase is a dextranase.

14. Textiles and textile products as described in paragraphs 1 to 12 whereby the linker molecule is a hyaluronic acid based biopolymer and the hydrolase is a hyaluronidase.

15. Textiles and textile products as described in paragraphs 1 to 12 whereby the linker molecule is a protein- or peptide-based polymer and the hydrolase is a protease or an endopeptidase, respectively.

16. Medical and sanitary textile, textile products and implants that are engineered with biologically active substances as described in paragraphs 1 to 15 whereof bioactive non-linker molecular species are released by hydrolases by catalytically cleaving the linker polymer.

17. Functional textile engineered according to paragraph 1 to 16 whereby the biologically active molecules suppress the proliferation of bacteria or fungi.

18. Yarn, textile and textile products as described in paragraphs 1 to 5 by linker molecules, the addition of which alters the physical and chemical properties of the textile material.

19. Functionalized linker polymers consisting of a polymer as described in paragraph 3 and having additional secondary functional groups such as carboxyl-, amino-, or thiol functions, that allow, singular or in combination, timed release of bioactive molecules.

20. Yarn, textile and textile products as described in paragraphs 1 to 5 and paragraphs 18 and 19, wherein the linker molecule is a biopolymer with negative charges and the bioactive agents are positive charged metal ions (for example as released from sputtered metallic deposits).

21. Yarn, textile and textile products as described in paragraphs 1 to 5 and paragraphs 18 and 20, wherein the linker molecule is a biopolymer with negative charges and the bioactive agents are positive charged silver ions (for example as released from sputtered silver deposits).

22. Yarn, textile and textile products wherein the linker molecule is a negatively charged photoactive biopolymer as described in paragraphs 1 to 5 and paragraphs 18 and 20, whereby the biologically active non-linker molecular species is lysozyme and both lysozyme and metal ions are used in combination to inhibit bacterial proliferation.

Although the present invention has been described in considerable detail with reference to certain preferred versions thereof, other versions are possible. For example instead of using yarn and textile products as material substrate, the substrate may be of solid materials such as for instance metal oxides on metal or glass surfaces, on organic polymers and many other material substrates. Therefore, the spirit and scope of the appended paragraphs should not be limited to the description of the preferred versions contained herein.

The following examples document procedures, and attained product properties of polyester yarn, textile and textile products. Procedures are applicable with slight modifications to other natural and synthetic yarns and textile products including blended yarns and textile.

EXAMPLE 1

Synthesis of photolinker polymers: OptoDex A, OptoDex C and Cy3-OptoDex.
OptoDex A was prepared by partial thiocarbamoylation of the amino groups of aminodextran – a 40 kDalton dextran with up to 80 mol amino functions per mol dextran as obtained for instance from Molecular Probes, with 3-(trifluoromethyl)-3-(m-isothiocyanophenyl) diazirine. OptoDex C was synthesized by derivatization of OptoDex A with glutaranhydride. Cy3-OptoDex was prepared by treatment of OptoDex A with the monofunctional N-hydroxysuccinimide ester of Cy3 cyanine dye (a product of Amersham). OptoDex A, OptoDex C and Cy3-OptoDex are thus linker polymers which are multiple substituted with both, the photoactive chemical species and amino functions (OptoDex A), carboxy functions (OptoDex C) or a fluorescent dye Cy3-OptoDex.

EXAMPLE 2

Textile pre-treatment and coating with photolinker polymers.
Commercial synthetic polyester yarn shows low water adsorption and wetting properties are not favourable for treatment with aqueous systems. As a consequence of the low water binding capacity, the surfaces did not sufficiently wet to achieve adsorptive binding of the photolinker polymer. Oxygen plasma treatment for 3 min (250 Watt, Oxygen pressure, 250 mτ) resulted in good wetting of polyester textile fabric. Wetting properties of functionalised polyester textile was improved upon treatment of the textile with the photolinker polymer OptoDex A, OptoDex C or Cy3-OptoDex.

In one set of experiments, coating of polyester tissue with the photolinker polymer OptoDex was carried out with non-fluorescent OptoDex A and with the fluorescent OptoDex Cy3 using polyester textile sample pads (2 x 2 cm) produced by Bischoff-Textil, Switzerland. After oxygen plasma treatment, tissue samples were incubated in aqueous solutions containing either OptoDex A or OptoDex Cy3. The samples were

rinsed with water, dried and exposed to light (4 min, 11 mW/ cm^2) for photoimmobilization. After photoimmobilization, excess OptoDex was removed by rinsing with phosphate buffered saline (PBS) containing 0.05% Tween 20, pH 7.4, followed by PBS, pH 7.4. (products purchased from Sigma) and water. The samples were then sonicated in deionized water and dried by centrifugation. Tissue samples were then investigated by light microscopy (textile appearance) and fluorescence microscopy (Cy3-OptoDex binding). Treatment of the textile with OptoDex A does not alter the appearance and texture of the sample (Figure 1A). Post-process dyeing of the fabric is shown in Figure 1B.

EXAMPLE 3

Photoimmobilization of alkaline phosphatase on woven polyester textile:

a) Optodex A was dissolved with PBS buffer (1:100 diluted) at a final concentration of 0.04 mg/ml, 0.2 mg/ml and 0.4 mg/ml respectively. Tissue samples (woven polyester, 8 x 9 cm^2) were treated with oxygen plasma and dipped in the OptoDex A solution for 1 hour at room temperature. Tissue samples were rinsed with bidistilled water, dried in vacuum for 1 h (5 x 10^{-2} mbar) and stored vacuum packed at -20°C till used.

b) Photoimmobilization of alkaline phosphatase: Alkaline phosphase was dissolved in PBS (1:100 diluted containing 10% ethanol) and applied to OptoDex A coated tissue samles (1.0 µg/100 µl applied to 1 cm^2 textile). Identically treated non OptoDex A-coated tissue samples served as controls (8 replicate for each sample). After drying for 3 h in vacuum (1 h at 20 mbar, followed by 2 h at 5 x 10^{-2} mbar), chips were irradiated for 4 min with an Oriel light source (350 nm, 11 mW/cm^2). All samples were rinsed with permanent solvent stirring with the following media and incubation times: 3 times 5 min PBS / Tween 20, 0.05%, pH, 7.4, 3 times 5 min PBS, pH 7.4 and 3 times 5 min H_2O.

c) Assay of alkaline phosphatase activity on modified tissue: The enzymatic activity of alkaline phosphatase was determined using the Phosphatase Substrate Kit as purchased from Pierce Chemicals. The enzyme substrate solution was prepared by dissolving one PNPP tablet in 8 ml bidistilled water and 2 ml DEA buffer. Enzyme treated and control tissue samples were placed in individual Falcon plate wells (48 well Falcon plate) and the substrate solution (400 µl/chip) was added and incubated for 30 min at 37 °C. The enzymatic reaction was stopped by addition 2 N NaOH (200 µl/chip) and the reaction solution was transferred to a

microtiter plate (200 µl/chip/well). For assay quantitation, colour development was measured on an ELISA reader (Spectra max 340) by registrating the absorption at 405 nm.

EXAMPLE 4

Enzymatic activity of lysozyme onto woven polyester textile

a) Optodex A was dissolved with PBS buffer (1:100 diluted) at a final concentration of 0.1 mg/ml. Tissue samples (woven polyester, 8 x 9 cm^2) were treated with oxygen plasma and dipped in the OptoDex A solution for 1 hour at room temperature. Tissue samples were rinsed with bidistilled water, dried in vacuum for 1 h (5 x 10^{-2} mbar) and stored vacuum packed at -20°C till used.

b) Photoimmobilization of lysozyme: Lysozyme from egg white (Sigma L 6876) was dissolved with PBS (1:100 diluted containing 10% ethanol) and applied to OptoDex A coated tissue samples (6.4 µg / 100 µl, applied to 1 cm^2 textile). Identically treated non OptoDex A-coated tissue samples served as controls (8 replicate for each sample). After drying for 3 h in vacuum (1 h at 20 mbar, followed by 2 h at 5 x 10-2 mbar), chips were irradiated for 4 min with an Oriel light source (350 nm, 11 mW/cm2). All samples were rinsed with permanent solvent stirring with the following media and incubation times: 3 times 5 min PBS / Tween 20, 0.05%, pH, 7.4, 3 times 5 min PBS, pH 7.4 and 3 times 5 min H2O.

c) Enzymatic activity of lysozyme on tissue: Enzymatic activity was determined with EnzChek Lysozyme Assay Kit (Molecular Probes). The assay is based on the catalytic property of lysozyme to break cell wall components of certain bacteria. One component of the assay is fluorescent-labelled *Micrococcus lysodeikticus* bacteria. Upon cell lysis the fluorophores are released and fluorescence can be measured in solution. Lysozyme coated tissue samples were individually placed in Falcon plate wells (48 well plates), the original enzyme substrate solution was diluted by a factor of 40 and applied to the tissue samples (400 µl/chip). After incubation for indicated lengths of time at 37°C at 80% humidity, substrate solutions were transferred to fluoro-microtiterplate for fluorescent signal measurement (200 µl/well). Signal intensities were registered with a Luminescence Spectrometer LS 50B (λ_{ex} = 485 nm and λ_{em} = 530 nm).

EXAMPLE 5

Dextranase catalysed release of OptoDex tethered lysozyme

Photoimmobilization of lysozyme modified polymer samples was carried out as described in the example 4 and surfaces were rinsed with permanent solvent stirring with the following media and incubation times: 3 times 5 min PBS / Tween 20, 0.05%, pH. 7.4, 3 times 5 min PBS, pH 7.4 and 3 times 5 min H_2O. Before measuring the enzymatic activity, OptoDex tethered lysozyme was treated with the enzyme dextranase. Dextranase was dissolved in 0.1 M sodium phosphate buffer pH 6.8 in (10 µg/ml), 60 µl were applied per well and the mixture was incubated during 30 min at 37° C. Total lysozyme activity was determined as described in example 4. The results are summarized in the Table below

Dextranase catalysed release of OptoDex tethered lysozyme

	Lysozyme activity (Fluorescence intensity: arbitrary units)		
Lysozyme assay incubation time	Without dextranase treatment	With dextranase treatment	Difference
1 hour	73	79	6
24 hours	273	608	335
48 hours	399	795	396
180 hours	500	812	312

EXAMPLE 6

Combined functionalization of textile with metallic silver and lysozyme:

a) Method of deposition of metals and dielectrics to a substrate in a vacuum chamber with ionized gases, e.g. argon, and effect of such deposited silver on bacterial proliferation.

Polyester tissue samples (woven polyester, 8 x 9 cm^2) were placed in a vacuum chamber and the textile substrate was evacuated to a pressure of less than 5×10^{-5} mbar. A plasma of argon ions is generated by applying a voltage of 400 Volts to a silver target and introduction of argon to a pressure of 5×10^{-3} mbar. Silver was deposited to the substrate for 12 sec. to get a deposit thickness of approx. 20 nm. Bioactivity of such treated textile was investigated by analyzing the cell proliferation of *Staphylococcus aureus* and *Klebsiella pneumoniae* after

incubation of impregnated textile at 37°C. The table below lists the change in cell count (log) after 24 hours incubation (mean values of 3 experimental series)

Bioactivity of silver treated polyester textile

Textile	Incubation time (hours)	*Staphylococcus aureus* Change of cell counts (log)	*Klebsiella pneumoniae* Change of cell counts (log)
PES untreated	24	+ 3.0	+ 2.8
PES, Silver treated	24	- 0.5	- 1.2

b) Lysozyme functionalization of silver treated textile

Silver treated samples as described above were coated with OptoDex A, Optodex A being dissolved in PBS buffer (1:100 diluted) at a final concentration of 0.1 mg/ml. Tissue samples were dipped in the OptoDex A solution for 1 hour at ambient temperature. Tissue samples were rinsed with bidistilled water, dried in vacuum for 1 h (5×10^{-2} mbar) and stored vacuum packed at -20°C till used.
Lysozyme was photoimmobilized by procedures analogous to the description in example 4, paragraph b, and the lysozyme activity was assayed as detailed in paragraph c, example 4. Long-term lytic activity of covalent immobilized lysozyme is retained. Due to quenching of the released fluorescence by the presence of metallic silver, the recorded fluorescence intensities are decreased . The combined treatment of textile with metallic silver and lysozyme results in a functionalized textile that affects bacterial by cell wall lysis (non diffusilbe lysozyme) and by the inhibition of vital bacterial cell function with silver ions.

Claims

1. A method of providing a yarn or textile product with a desired property which comprises:

contacting a linker molecule comprising two or more activatable chemical groups with a yarn or textile product, and a non-linker molecule having a desired property;

activating the activatable chemical groups of the linker molecule to cause covalent attachment of the linker molecule to the yarn or textile product and the non-linker molecule, thereby attaching the non-linker molecule to the yarn or textile product by means of the linker molecule, and providing the yarn or textile product with the property of the non-linker molecule.

2. A method according to claim 1, wherein the linker molecule is contacted with the yarn or textile product before the non-linker molecule.

3. A method according to claim 1 or 2, wherein the non-linker molecule is a solvent, a synthetic or natural chemical, a synthetic or natural dye, a synthetic polymer, a biopolymer, a biomolecule, a biologically active molecule, a synthetic or natural vitamin or hormone, or any combination thereof.

4. A method according to any preceding claim, wherein the non-linker molecule is an enzyme (such as lysozyme), a growth factor, an anti-microbial agent, an antibiotic, a fungicide, an agent capable of suppressing the proliferation of bacteria or fungi, or any combination thereof.

5. A method according to any preceding claim, wherein the linker molecule further comprises one or more functional groups having a desired property different to the property of the non-linker molecule, so that covalent attachment of the linker molecule to the yarn or textile product additionally provides the yarn or textile product with the property of the, or each functional group.

6. A method of providing a yarn or textile product with a desired property which comprises:

contacting a linker molecule comprising one or more activatable chemical groups, and one or more functional groups having a desired property, with a yarn or textile product;

activating the activatable chemical group or groups of the linker molecule to cause covalent attachment of the linker molecule to the yarn or textile product, thereby providing the yarn or textile product with the property of the functional group of the linker molecule.

7. A method according to claim 5 or 6, wherein the, or each functional group is a positively charged group at neutral pH (such an amino group), a negatively charged group at neutral pH (such as a carboxyl group), a thiol group, or a dye such as a fluorescent dye.

8. A method according to claim 7, wherein the, or each functional group is negatively charged, and the method further comprises contacting the yarn or textile product with positively charged metal ions, preferably silver ions, to bind the metal ions to the functional group or groups.

9. A method according to claim 8, wherein the metal ions are contacted with the yarn or textile product before the linker molecule.

10. A method according to any preceding claim, wherein the linker molecule is multiply substituted with activatable chemical groups.

11. A method according to any preceding claim, wherein activation of the, or each activatable chemical group of the linker molecule generates a carbene intermediate.

12. A method according to any preceding claim, wherein the, or each activatable chemical group is activated with actinic energy and converts to a highly reactive intermediate.

13. A method according to any preceding claim, wherein the, or each activatable chemical group of the linker molecule is thermochemically or photochemically activatable.

14. A method according to any preceding claim, wherein the linker molecule comprises a natural or synthetic polymer, preferably a biopolymer.

15. A method according to claim 14, wherein the linker molecule comprises a protein, peptide, or polysaccharide.

16. A method according to claim 14, wherein the linker molecule comprises a dextran-based polymer.

17. A method according to any preceding claim, wherein the linker molecule comprises a cleavage site which is cleaved under predetermined conditions to release the non-linker molecule or functional group from the yarn or textile product.

18. A method according to claim 17, wherein the linker molecule comprises a target for a hydrolytic enzyme to allow enzyme-induced, or biosystem-induced release of the non-linker molecule or functional group.

19. A method according to claim 17 or 18, wherein the linker molecule comprises a substrate for an endoglycosidase, or an endopeptidase.

20. A method according to claim 18, wherein the linker molecule is a dextran-based biopolymer which comprises a target for a dextranase.

21. A method according to claim 18, wherein the linker molecule is a hyaluronic acid-based biopolymer which comprises a target for a hyaluronidase.

22. A method according to claim 18, wherein the linker molecule is a protein-based polymer which comprises a target for a protease.

23. A method according to claim 18, wherein the linker molecule is a peptide-based polymer which comprises a target for an endopeptidase.

24. A method according to any preceding claim, wherein the textile product is of natural or synthetic origin, a blend of synthetic yarns, or a blend of natural and synthetic yarns.

25. A method according to any preceding claim, wherein the yarn or textile product is pre-treated to improve its wetting properties.

26. A method according to claim 25, wherein the yarn or textile product is pre-treated with oxygen plasma.

27. A method according to claim 25 or 26, wherein the yarn or textile product is synthetic polyester.

28. A linker molecule as defined in any of claims 1, 5 to 8, or 10 to 23.

29. Use of a linker molecule as defined in any of claims 1, 5 to 8, or 10 to 23 to covalently attach a non-linker molecule having a desired property and/or a functional group having a different desired property to a yarn or textile product, thereby providing the yarn or textile product with the desired property or properties.

30. A yarn or textile product covalently attached, by means of a linker molecule, to a non-linker molecule having a desired property, thereby providing the yarn or textile product with the desired property.

31. A yarn or textile product according to claim 30, wherein the non-linker molecule is a solvent, a synthetic or natural chemical, a synthetic or natural dye, a synthetic polymer, a biopolymer, a biomolecule, a biologically active molecule, a synthetic or natural vitamin or hormone, or any combination thereof.

32. A yarn or textile product according to claim 30 or 31, wherein the non-linker molecule is an enzyme (such as lysozyme), a growth factor, an anti-microbial agent, an antibiotic, a fungicide, an agent capable of suppressing the proliferation of bacteria or fungi, or any combination thereof.

33. A yarn or textile product according to any of claims 30 to 32, wherein the linker molecule comprises one or more functional groups having a different desired property to that of the non-linker molecule, thereby additionally providing the yarn or textile product with the different desired property.

34. A yarn or textile product covalently attached to a linker molecule, the linker molecule comprising one or more activatable chemical groups to allow covalent attachment of a non-linker molecule having a desired property to the linker molecule and thereby provide the yarn or textile product with the desired property.

35. A yarn or textile product according to claim 34, wherein activation of the, or each activatable chemical group of the linker molecule generates a carbene intermediate.

36. A yarn or textile product according to claim 34 or 35, wherein the, or each activatable chemical group converts to a highly reactive intermediate when activated with actinic energy.

37. A yarn or textile product according to any of claims 34 to 36, wherein the, or each activatable chemical group of the linker molecule is thermochemically or photochemically activatable.

38. A yarn or textile product according to any of claims 34 to 37, wherein the linker molecule further comprises one or more functional groups having a desired property, thereby providing the yarn or textile product with the desired property.

39. A yarn or textile product covalently attached to a linker molecule, the linker molecule comprising one or more functional groups having a desired property, thereby providing the yarn or textile product with the desired property.

40. A yarn or textile product according to claim 33, 38, or 39, wherein the, or each functional group is a positively charged group at neutral pH (such an amino group), a negatively charged group at neutral pH (such as a carboxyl group), a thiol group, or a dye such as a fluorescent dye.

41. A yarn or textile product according to claim 40, wherein the, or each functional group is negatively charged, and the yarn or textile product further comprises positively charged metal ions, preferably silver ions, bound to the functional group or groups.

42. A yarn or textile product according to any of claims 30 to 41, wherein the linker molecule comprises a natural or synthetic polymer, preferably a biopolymer.

43. A yarn or textile product according to claim 42, wherein the linker molecule comprises a protein, peptide, or polysaccharide.

44. A yarn or textile product according to claim 43, wherein the linker molecule comprises a dextran-based polymer.

45. A yarn or textile product according to any of claims 30 to 44, wherein the linker molecule comprises a cleavage site which is cleaved under predetermined conditions to allow release of the non-linker molecule or functional group from the yarn or textile product.

46. A yarn or textile product according to claim 45, wherein the linker molecule comprises a target for a hydrolytic enzyme to allow enzyme-induced, or biosystem-induced release of the non-linker molecule.

47. A yarn or textile product according to claim 46, wherein the linker molecule comprises a substrate for an endoglycosidase, or an endopeptidase.

48. A yarn or textile product according to claim 46, wherein the linker molecule is a dextran-based biopolymer which comprises a target for a dextranase.

49. A yarn or textile product according to claim 46, wherein the linker molecule is a hyaluronic acid-based biopolymer which comprises a target for a hyaluronidase.

50. A yarn or textile product according to claim 46, wherein the linker molecule is a protein-based polymer which comprises a target for a protease.

51. A yarn or textile product according to claim 46, wherein the linker molecule is a peptide-based polymer which comprises a target for an endopeptidase.

52. A yarn or textile product according to any of claims 30 to 51 which is of natural or synthetic origin, a blend of synthetic yarns, or a blend of natural and synthetic yarns.

53. A composition comprising a yarn or textile product, a linker molecule as defined in any of claims 1, 5 to 8, or 10 to 23, and optionally a non-linker molecule as defined in claim 31 or 32.

Figure 1 A

Cy3 OptoDex OptoDex A

Figure 1 B

OptoDex Cy3 OptoDex A

Figure 2

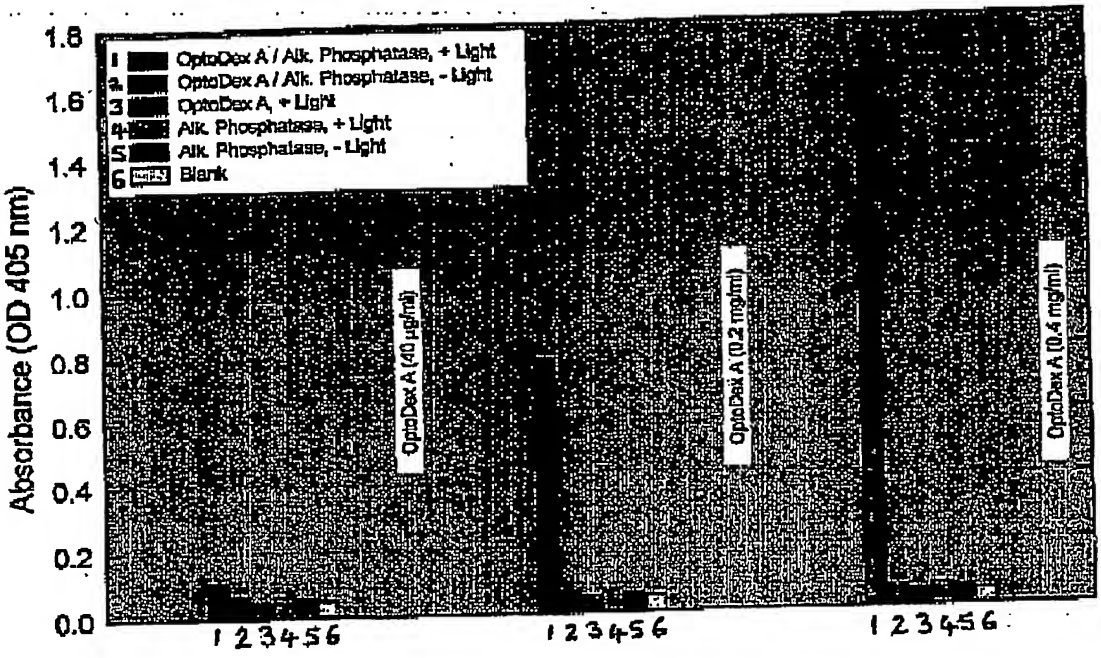

1 OptoDex A / Alk. Phosphatase, + Light
2 OptoDex A / Alk. Phosphatase, - Light
3 OptoDex A, + Light
4 Alk. Phosphatase, + Light
5 Alk. Phosphatase, - Light
6 Blank
Absorbance (OD 405 nm)
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
OptoDex A (40 µg/ml)
OptoDex A (0.2 mg/ml)
OptoDex A (0.4 mg/ml)
1 2 3 4 5 6
1 2 3 4 5 6
1 2 3 4 5 6

Figure 3

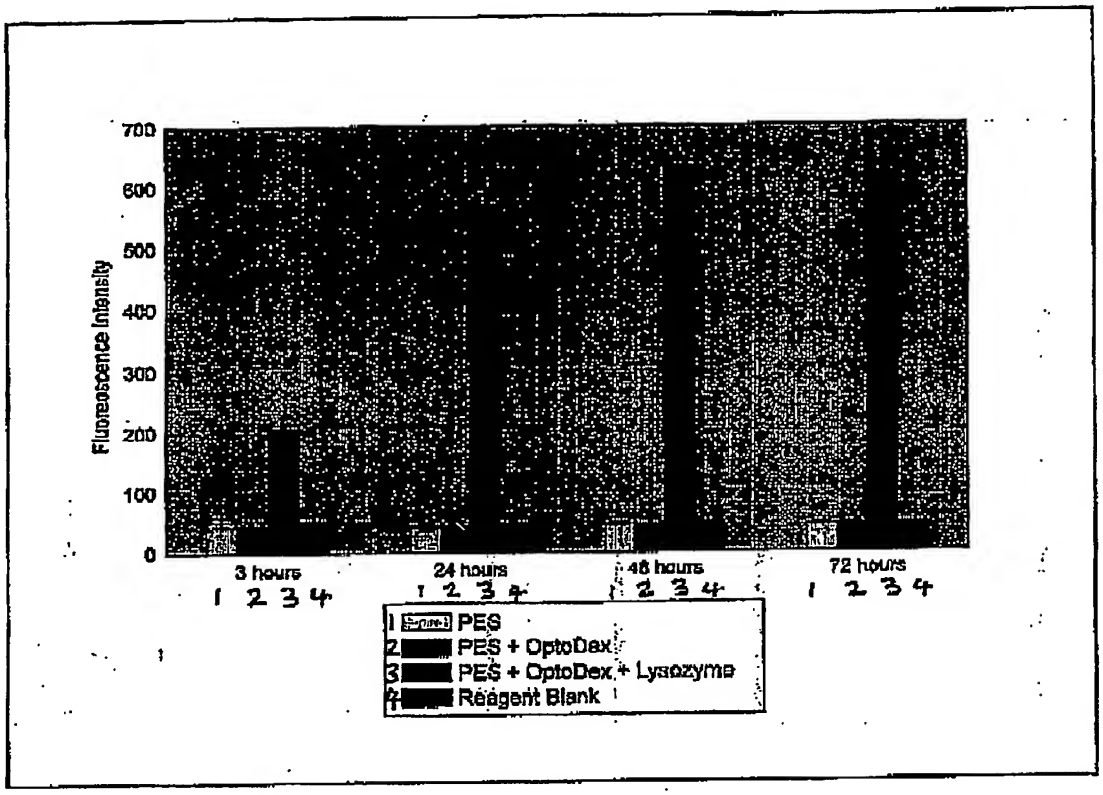
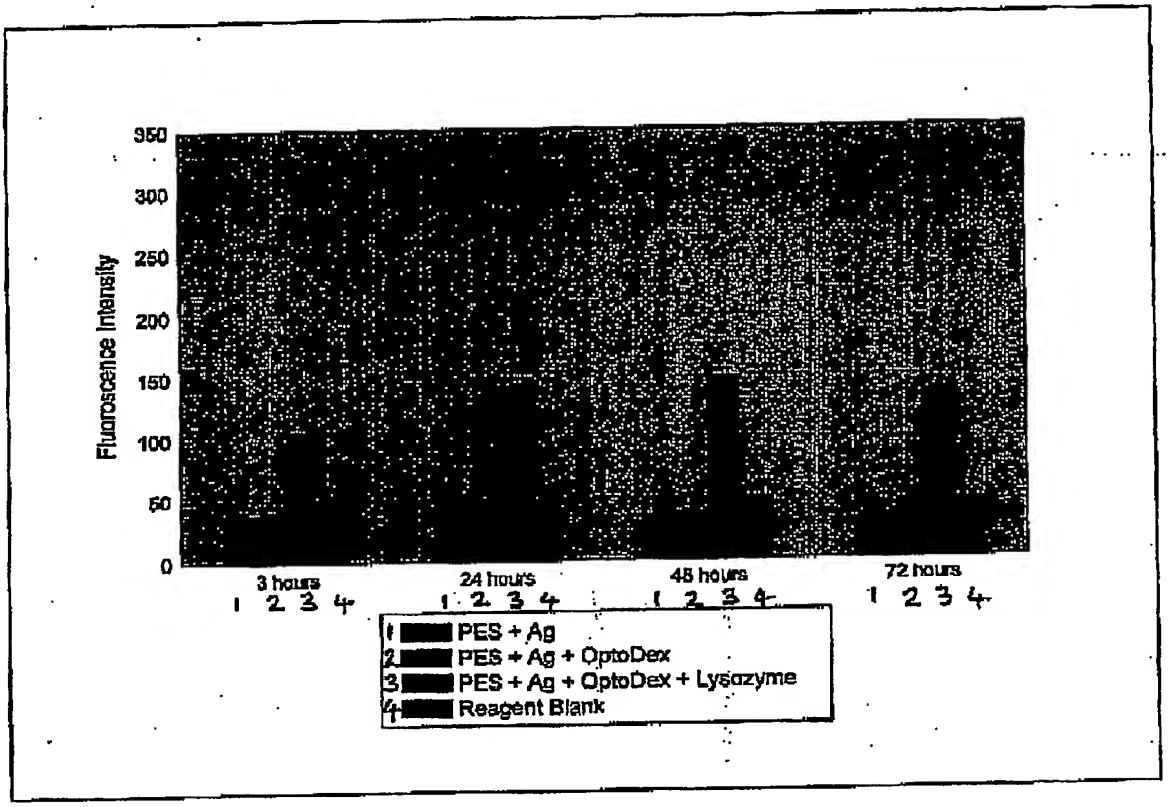

Fluorescence Intensity
700
600
500
400
300
200
100
0
3 hours
1 2 3 4
24 hours
1 2 3 4
48 hours
1 2 3 4
72 hours
1 2 3 4
1 PES
2 PES + OptoDex
3 PES + OptoDex + Lysozyme
4 Reagent Blank

Figure 4


Fluorescence Intensity
350
300
250
200
150
100
50
0
3 hours
24 hours
48 hours
72 hours
1 2 3 4
1 PES + Ag
2 PES + Ag + OptoDex
3 PES + Ag + OptoDex + Lysozyme
4 Reagent Blank